

(19)



Europäisches Patentamt
European Patent Office
Office européen des brevets



(11)

EP 0 726 078 B1

(12)

EUROPEAN PATENT SPECIFICATION

(45) Date of publication and mention
of the grant of the patent:
05.09.2001 Bulletin 2001/36

(51) Int Cl.7: **A61L 17/00, D01F 6/06**

(21) Application number: **96300904.8**

(22) Date of filing: **09.02.1996**

(54) **In-line annealing of sutures**

Inlinie-Glühen von Nähten

Recuit en ligne de sutures

(84) Designated Contracting States:
AT BE ES FR GB IT NL

(30) Priority: **10.02.1995 US 386617**

(43) Date of publication of application:
14.08.1996 Bulletin 1996/33

(73) Proprietor: **ETHICON, INC.**
Somerville, NJ 08876 (US)

(72) Inventor: **Lennard, David J.**
Flemington, NJ 08822 (US)

(74) Representative: **Mercer, Christopher Paul et al**
Carpmaels & Ransford
43, Bloomsbury Square
London WC1A 2RA (GB)

(56) References cited:

EP-A- 0 415 783	EP-A- 0 526 759
DE-A- 2 037 813	FR-A- 2 361 119
US-A- 4 911 165	US-A- 5 269 807

EP 0 726 078 B1

Note: Within nine months from the publication of the mention of the grant of the European patent, any person may give notice to the European Patent Office of opposition to the European patent granted. Notice of opposition shall be filed in a written reasoned statement. It shall not be deemed to have been filed until the opposition fee has been paid. (Art. 99(1) European Patent Convention).

Description**FIELD OF THE INVENTION**

5 **[0001]** This invention relates to the field of suture manufacture and more specifically it relates to an in-line process for extruding, drawing and annealing polypropylene sutures.

BACKGROUND OF THE INVENTION

10 **[0002]** Surgical sutures made from polypropylene have been successfully used by the medical profession for more than twenty years. One of the first commercially successful polypropylene suture to gain wide acceptance was described in U.S. Patent 3,630,205 to Gregory J. Listner. Listner disclosed a process for manufacturing polypropylene suture that comprised the steps of drawing an extruded polypropylene suture to about 6.6 times its original extruded length and then relaxing or shrinking the monofilament to between about 91 to 76 percent of the stretched length.

15 **[0003]** Lennard et al. in U.S. Patent 4,911,165 later disclosed an improved process for making polypropylene sutures that have increased compliance, limpness or flexibility to make the polypropylene sutures easier to handle and improved their knot security. The process described by Lennard comprised extruding polypropylene through an orifice and quenching the extrudate to form a filament. The filament was first drawn about 6X to 7X then drawn a second time from about 1.06X to about 1.5X. Finally the filament was collected and heat relaxed offline to effect a linear shrink and heat set. The heat relaxation as disclosed by Lennard is performed by placing the filament on a rack in an annealing oven and allowing the filament to shrink from about 16 to about 35 percent of the original length of the filament. The annealing is carried out at a temperature within the range of from about 135°C to about 152°C, for a period of time sufficient to permit the filament to shrink and heat set normally 5 to about 40 minutes.

20 **[0004]** As good as the fibers are that may be produced from the processes disclosed by Listner and Lennard there is room for improvement in these processes. In particular it would be desirable to eliminate the separate annealing step performed on the filaments after the filament has been draw to stream line the suture product and handling.

25 **[0005]** Thus it is an object of the present invention to provide a process for producing polypropylene suture that eliminates the rack annealing of polypropylene sutures. This and other objects and advantages of the present invention will be obvious to those skilled in the art from the following specification.

SUMMARY OF THE INVENTION

30 **[0006]** We have discovered an in-line process for producing a polypropylene suture comprising the steps of (a) extruding melted polypropylene resin through an orifice and rapidly quenching the melted polypropylene resin to produce a filament; (b) drawing the filament in the range of from about 4X to about 7.5X in a first drawing zone to produce a drawn filament; (c) drawing the singly drawn filament in a second drawing zone in the range of from about 1.0X to about 2.5X while in a first heated zone being maintained at a temperature in the range of from about 30°C to about 160°C, to form a doubly drawn filament; (d) relaxing the doubly drawn filament in the range of from about 0.75X to about 0.95X, in a second heated zone being maintained at a temperature in the range of from about 100°C to about 180°C, to form an annealed polypropylene suture.

BRIEF DESCRIPTION OF THE FIGURES

35 **[0007]** The FIGURE is a side elevation, partially schematic of an apparatus suitable for carrying out the process of the present invention.

DETAILED DESCRIPTION OF THE INVENTION

40 **[0008]** As used herein the term polypropylene shall include isotactic and syndiotactic polypropylene and blends thereof, as well as, blends composed predominately of isotactic or syndiotactic polypropylene blended with heterotactic polypropylene and polyethylene (such as is described in U.S. Patent 4,557,264 issued December 10, 1985 assigned to Ethicon, Inc. hereby incorporated by reference) and copolymers composed predominately of propylene and other alpha-olefins such as ethylene (which is described in U.S. Patent 4,520,822 issued June 4, 1985 assigned to Ethicon, hereby incorporated by reference). The preferred method for preparing the flexible polypropylene sutures of the present invention utilizes as the raw material pellets of isotactic polypropylene homopolymer having a weight average molecular weight of from about 260,00 to about 420,000. Polypropylene of the desired grade is commercially available in both powder and pellet form.

55 **[0009]** Referring to the FIGURE, there is shown an apparatus that is suitable for carrying out the present invention.

An extruder 10 is terminated at one end with an extrusion die 12. A longitudinal extruder screw is mounted for rotation within the barrel 16 and is driven by a variable speed motor 18 through a gear 20. Polypropylene pellets are introduced into the extruder through hopper 22 which communicates with the barrel 16. In normal operation of the extruder 10, the feeding zone 24 of the extruder is maintained at a temperature in the range of from about 140°C to about 200°C, the transition zone 26 is maintained at a temperature in the range of from about 170°C to about 220°C, and the pump block 30, block 28 and die 12 are maintained at a temperature in the range of from about 170°C to about 225°C. A pump 33 driven by a motor 32, pumps the molten polypropylene through spinneret orifices in the die 12 to form a plurality of filaments 31 (for simplicity only one filament is shown in the FIGURE). The filament 31 is extruded into quench bath 34. The quench bath 34 is filled with a liquid heat exchange medium. The surface of the liquid in the quench bath 34 is preferably not more than a few centimeter below the die 12 in order to achieve rapid cooling of the extruded filament 31. The quench bath 34 is maintained at a temperature below 50°C and preferably the quench bath 34 is maintained at about room temperature. The filament 31 enters the quench bath 34 and travels around idler roll 36 in the quench bath 34 and then up out of the quench bath 34 to another idle roller 35 then to the first godet 37 in the first drawing zone 2. In the first drawing zone 2 the filament 31 is drawn in the range of from about 5X to 7.5X its original length. The filament 31 may be drawn incrementally or in several discrete steps in the first drawing zone 2. The drawing will preferably be performed in a first heated zone 41 (such as a heated cabinet, oven, or by using heated godets). The temperature of the first heated zone will preferably be in the range of from about 30°C to about 170°C. Most preferably the first and second godet will be maintained at a temperature in the range of from about 40°C to 140°C. The filament 31 will remain in the first heated zone 41 generally only a short time preferably in the range of from about 0.1 seconds to about 10 seconds.

[0010] In the preferred embodiment of the invention shown in the attached Figure, the filament 31 is drawn by a first godet 37 and a second godet 42. The first godet 37 includes a main roll 38 and an air bearing 40. The first godet 37 is rotated at a peripheral speed that is equal to or slightly higher than the speed at which the filament 31 is extruded from the die orifice 12. The first godet 37 may be combined with a pinch roller (not shown) to assure the filament 31 does not slip in the subsequent drawing to the extruded filament 31. The first draw of the extruded filament 31 will be performed by feeding the extruded filament 31 from the first godet 37 to second godet 42 which includes a main roll 43 and an air bearing 44. The second godet 42 is rotated at a peripheral speed that is in the range of from about 5X to about 7.5X of the speed of the first godet 37.

[0011] The filament 31 then passes into a second drawing zone 4, where the filament 31 is drawn again in the range of from about 1.0X to about 2.5X while in a second heated zone 46. The filament 31 may be drawn incrementally or in one or more discrete steps in the second drawing zone 4. The drawing will be performed in a second heated zone 46. The temperature of the second heated zone 46 will be in the range of from about 30°C to about 180°C, preferably in the range of from about 75°C to about 140°C. The filament 31 will remain in the second heated zone 46 generally only a short time preferably in the range of from about 0.1 seconds to about 10 seconds.

[0012] In the preferred embodiment of the invention shown in the attached Figure, the filament 31 passes through a second heated zone 46 to a third godet 50. The second heated zone 46 is preferably an orienting oven 48 that is maintained at a temperature of in the range of from about 30°C to about 180°C, preferably in the range of from about 75°C to about 140°C and most preferably in the range of from 120°C to about 140°C. The filament 31 is drawn in the range of from about 1X to about 2X, while traveling from the second godet 42 to the third godet 50 in the second heated zone 46. The third godet 50 includes a main roll 51 and an air bearing 52, that are rotating at a peripheral speed of about 1X to about 2.5X of the peripheral speed of the second godet 42. Preferably the draw ratio will be in the range of from about 1.06X to about 1.9X.

[0013] The filament 31 then passes from the second drawing zone 4 into an annealing zone 6, where the filament 31 is annealed and allowed to shrink. In the annealing zone 6 the filament 31 is placed in a third heated zone 54 that is maintained at a temperature in the range of from about 100°C to about 180°C wherein the filament is allowed to shrink in the range of from about 5 percent to about 35 percent and preferably from about 5 to about 25 percent of the filament original length. The filament 31 may be allowed to shrink incrementally or in one or more discrete steps in the third heated zone 54. The filament 31 will remain in the third heated zone 54 for a short time generally in the range of from about 0.1 to about 20 seconds and preferably in the range of from about 0.1 seconds to 5 seconds.

[0014] In the preferred embodiment of the present invention shown in the attached FIGURE, the filament 31 then passes through a third heated zone 54 to a fourth godet 56. The heated zone 54 is preferably an annealing oven 60, that is maintained at a temperature of in the range of from about 100°C to 180°C. The filament 31 is then allowed to shrink in the range of from about 75 percent to about 95 percent of its original length. The fourth godet 56 includes a main roll 57 and an air bearing 58, that are rotating at a peripheral speed of about 0.75X to about 0.95X of the peripheral speed of the third godet 50. Preferably the relaxation ratio will be in the range of from about 0.8X to about 0.9X. After passing around the fourth godet 56, the filament 31 may then be fabricated into sutures.

[0015] The overall draw ratio, that is, the difference between the peripheral speed of the fourth godet 56 and the first godet 37, will ordinarily be from about 6X to about 8X and preferably the total draw ratio will be in the range of from

about 6.4X to about 6.7X.

[0016] The residence time of filament 31 within any of the heated zones can be optimized to improve fiber properties. The overall residence time that filament 31 is present in the second and third heated zones will preferably be in the range of from about 2 seconds to about 50 seconds and most preferably in the range of from about 4 seconds to about 20 seconds. The residence time can be increased with longer ovens or by having multiple wraps of the fiber in the oven.

[0017] The filaments of the present invention may be fabricated into surgical sutures in accordance with customary procedures without additional annealing. The filaments coming off the fourth godet 56 may be inspected and cut to length using an in-line cutting device. In a fully automated line the cut lengths of suture would then be swaged. One suitable device for automatically cutting and swaging is disclosed in EP-A-0 667 120.

[0018] Alternatively for convenience the filament 31 coming off the fourth godet 56 may proceed to a windup station 62 and be wound onto spools 70 for later use. The filament 31 may be stored before further processing to allow the filament 31 to achieve complete stability of all its properties such as modulus (which may continue to rise for 18 to 120 hours after manufacture). Those skilled in the art can readily determine if any optimum storage time exist before further processing.

[0019] If the filament 31 is stored on spools 70 the filament 31 may acquire a tendency to bend or curl in a circular pattern commonly referred to as a filament memory. To facilitate further processing of the filament 31 it may be desirable to expose the filament to a fourth heated zone to remove the memory as the filament 31 is further handled and inspected. In one embodiment of the present invention the filament 31 would be removed from the spool 70 and exposed to the fourth heated zone maintained at a temperature in the range of from about 50 °C to about 80°C. The filament 31 would be exposed to the fourth heated zone 72 for a very short period of time preferably in the range of from about 24 hours to about 2 hours. In the fourth heated zone because of the low temperature and short time of exposure of the filament 31 to the temperature no appreciable shrinkage of the filament 31 should occur.

[0020] The following non-limiting examples are further provided to illustrate the practice of the present invention.

EXAMPLE

[0021] Dyed isotactic polypropylene having a melt flow of 3-5 as determined by ASTM D1238 was used to produce surgical sutures under the conditions set forth in Table 1 below.

TABLE 1

Sample No.	1	2	3	5	6
Filament Size	2	2	2/0	6/0	6/0
Feed Zone °C	160(320°F)	160(320°F)	160(320°F)	160(320°F)	160(320°F)
Transition Zone °C	186(366°F)	186(366°F)	186(355°F)	186(365°F)	186(365°F)
Pump °C	186(365°F)	186(366°F)	186(365°F)	199(391°F)	199(390°F)
Block °C	191(375°F)	191(375°F)	188(370°F)	204(400°F)	204(400°F)
Die °C	191(375°F)	191(375°F)	191(375°F)	204(400°F)	204(400°F)
Barrel MPa	10·3(1501psi)	10·4(1506psi)	10·3(1501psi)	10·4(1505psi)	10·4(1506psi)
Pump MPa	8·9(1286psi)	8·8(1277psi)	5·7(828psi)	4·5(657psi)	4·5(647psi)
Die MPa	1·26(183psi)	1·32(191psi)	2·84(412psi)	1·11(161psi)	1·12(162psi)
Pump RPM	11.2	24 ¹	6.1	4.8	4.8
Screw RPM	24.6	11.1 ¹	13.9	5	5
Godet 1 MPM/ °C (FPM/°F)	3·05/132 (10/270)	3·05/132 (10/270)	4·48/119 (14.7/246)	5·79/54 (19/130)	5·79/54 (19/130)
Godet 2 MPM/ °C (FPM/°F)	21·95/85 (72/185)	21·95/85 (72/185)	31·39/82 (103/180)	32·00/88 (105/190)	32·00/88 (105/190)
Orienting Oven °C	173(315°F)	129(265°F)	146(295°F)	129(265°F)	100(212°F)

TABLE 1 (continued)

Sample No.	1	2	3	5	6
Godet 3 MPM/ °C (FPM/°F)	25-16/77 (76/170)	23-16/77 (76/170)	35-66/88 (117/190)	44-81/77 (147/170)	44-81/77 (147/170)
Annealing Oven °C	129(265°F)	-	132(270°F)	100(212°F)	-
Godet 4 MPM	19.51(64FPM)	-	29.57(97FPM)	38.71(127FPM)	-

[0022] RPM is revolutions per minute.

FPM is feet per minute.

¹The original data page appears to have reversed these numbers.

MPM is metres per minute The surgical sutures 2 and 5 were wound on racks and annealed for 10-20 minutes in an annealing oven at 129-145°C. All the samples were sterilized and tested using the following test procedures. The data from these test are presented in Table 2

[0023] The characteristic properties of the sutures samples 1-6 were determined by conventional test procedures. The tensile properties (i.e., straight and knot tensile strengths and elongation) displayed herein were determined with an INSTRON Tensile Tester. The settings used to determine the straight tensile, knot tensile and break elongation were the following, unless indicated:

TABLE 2

	GAUGE LENGTH (cm)	CHART SPEED(cm)	CROSSHEAD SPEED (cm/min.)
STRAIGHT TENSILE	12.7	30.5	30.5
KNOT TENSILE	12.7	30.5	30.5
BREAK ELONGATION	12.7	30.5	30.5

[0024] The straight tensile strength was calculated by dividing the force to break by the initial cross-sectional area of the suture. The elongation at break was read directly from the stress-strain curve of the sample.

[0025] The knot tensile strength of a suture was determined in separate tests. The surgeon's knot was a square knot in which the free end was first passed twice, instead of once, through the loop, and the ends drawn taut so that a single knot was superimposed upon a compound knot. The first knot was started with the left end over the right end and sufficient tension was exerted to tie the knot securely.

[0026] The specimen was placed in the INSTRON Tensile Tester with the knot approximately midway between the clamps. The knot tensile strength was calculated by dividing the force required to break by the initial cross-sectional area of the fiber. The tensile strength values are reported in GPa and KPSI (PSI X 10³).

TABLE 3

Comparison of In-line and Rack Annealed Properties								
Sample No.	Size	Diameter mm	Tensile kg	Strength GPa	Knot. kg	Strength psi	Elongation %	Modulus GPa
1	2	0.5423 (21.35mils)	9.28 (20.46 lb)	394 (57150.00 psi)	6.06 (13.36 lb)	258 (37490.00 psi)	33.47	2620 (380.40 psi)
2	2	0.5441 (21.42 mils)	9.34 (20.58 lb)	393 (57080.00 psi)	5.89 (12.98 lb)	249 (36080.00 psi)	33.67	2351 (340.90 psi)
3	2/0	0.3221 (12.68 mils)	3.84 (8.46 lb)	469 (68060.00 psi)	2.93(6.45 lb)	357 (51760.00 psi)	40.28	1951 (283.10 psi)
4	6/0	0.0914 (3.60 mils)	0.49 (1.08 lb)	729 (105800.00 psi)	0.36(0.74 lb)	499 (72320.00 psi)	24.15	4342 (629.70 psi)

TABLE 3 (continued)

Comparison of In-line and Rack Annealed Properties								
Sample No.	Size	Diameter mm	Tensile kg	Strength GPa	Knot. kg	Strength psi	Elongation %	Modulus GPa
5	6/0	0.0919 (3.62 mils)	0.46 (1.05 lb)	704 (102100.00 psi)	0.35(0.78 lb)	526 (76240.00 psi)	32.51	2910 (422.00 psi)

Sample Numbers 1, 3 and 4 were produced by the inventive in-line annealing process described above. Samples 2 and 5 were produced by rack annealing the sutures following conventional manufacturing procedures. The data above demonstrates that the inventive process produces sutures that have suitable properties for being used as sutures.

Claims

1. An in-line process for producing a polypropylene suture comprising the steps of:

- (a) extruding melted polypropylene resin through an orifice and rapidly quenching the melted polypropylene resin to produce a filament;
- (b) drawing the filament in the range of from 4X to 7.5X in a first drawing zone to produce a drawn filament;
- (c) drawing the singly drawn filament in a second drawing zone in the range of from 1.0X to 2.5X while in a second heated zone being maintained at a temperature in the range of from 30°C to 160°C, to form a doubly drawn filament;
- (d) relaxing and annealing the doubly drawn filament in the range of from 0.75X to 0.95X, in a third heated zone being maintained at a temperature in the range of from 100°C to 180°C, to form an annealed polypropylene suture.

2. The process of claim 1 wherein the filament in the first drawing zone is exposed to a first heated zone being maintained at a temperature in the range of from 30°C to 170°C.

3. The process of claim 2 wherein the first heated zone is maintained at a temperature in the range of from 40°C to 140°C.

4. The process of any one of claims 1 to 3 wherein the second heated zone is maintained at a temperature in the range of from 75°C to 140°C.

5. The process of any one of claims 1 to 4 wherein the filament is drawn in a single step in the first draw zone.

6. The process of claim 5 wherein the filament is drawn by a first and a second heated godet.

7. The process of any one of claims 1 to 6 wherein the singly drawn filament is drawn in the range of from 1.06X to 1.9X in the second drawing zone.

8. The process of any one of claims 1 to 7 wherein the total draw ratio of the suture from drawing and relaxing is in the range of from 6 to 8.

9. The process of any one of claims 1-8 wherein the doubly drawn filament is relaxed in the range of from 0.8X to 0.9X.

Patentansprüche

1. In-line-Verfahren zur Herstellung eines Polypropylenmaterials, das die folgenden Stufen umfaßt:

- (a) Extrudieren von geschmolzenem Polypropylenharz durch eine Düse und rasches Abschrecken des geschmolzenen Polypropylenharzes zur Ausbildung eines Filaments;
- (b) Recken des Filaments im Ausmaß von 4x bis 7,5x in einer ersten Reckzone zur Ausbildung eines gereckten

Filaments;

(c) Recken des einfachgereckten Filaments in einer zweiten Reckzone im Ausmaß von 1,0x bis 2,5x, während es sich in einer zweiten Heizzone befindet, die auf einer Temperatur im Bereich von 30°C bis 160°C gehalten wird, um ein doppeltgerecktes Filament auszubilden;

(d) Entspannen und Tempern des doppeltgereckten Filaments im Ausmaß von 0,75x bis 0,95x in einer dritten Heizzone, die auf einer Temperatur im Bereich von 100°C bis 180°C gehalten wird, zur Ausbildung eines getemperten Polypropylennahtmaterials.

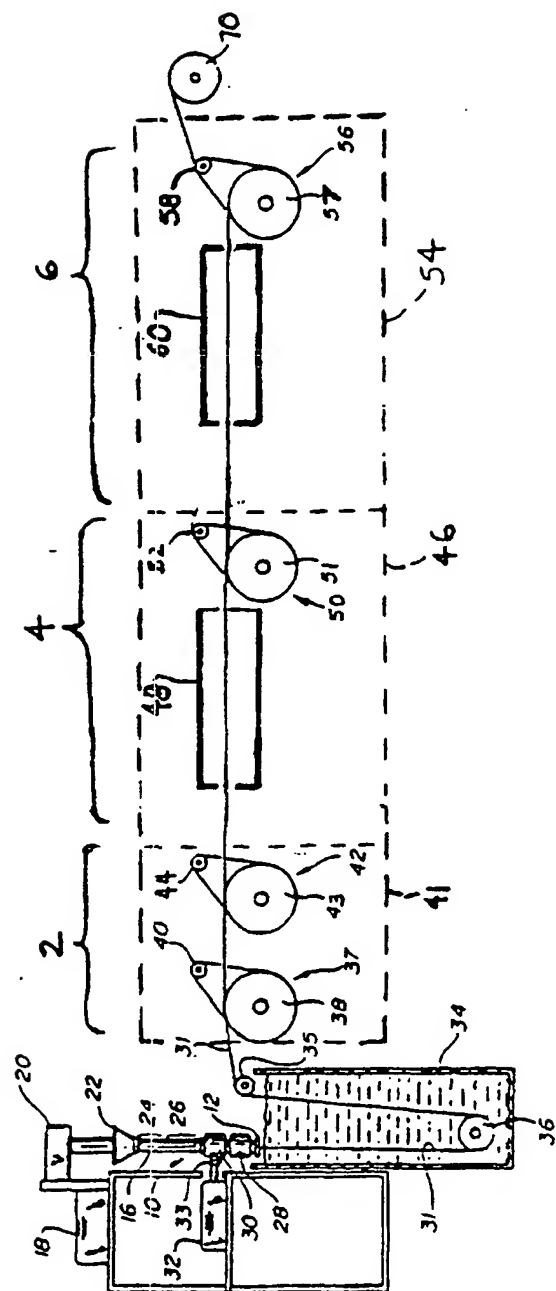
2. Verfahren nach Anspruch 1, worin das Filament in der ersten Reckzone einer ersten Heizzone ausgesetzt wird, die auf einer Temperatur im Bereich von 30°C bis 170°C gehalten wird.
3. Verfahren nach Anspruch 2, worin die erste Heizzone auf einer Temperatur im Bereich von 40°C bis 140°C gehalten wird.
4. Verfahren nach einem der Ansprüche 1 bis 3, worin die zweite Heizzone auf einer Temperatur im Bereich von 75°C bis 140°C gehalten wird.
5. Verfahren nach einem der Ansprüche 1 bis 4, worin das Filament in der ersten Reckzone in einer einzigen Stufe gereckt wird.
6. Verfahren nach Anspruch 5, worin das Filament mit einem ersten und einem zweiten erhitzten Streckwerk gereckt wird.
7. Verfahren nach einem der Ansprüche 1 bis 6, worin das einfachgereckte Filament in der zweiten Reckzone im Ausmaß von 1,06x bis 1,9x gereckt wird.
8. Verfahren nach einem der Ansprüche 1 bis 7, worin das Gesamtreckverhältnis des Nahtmaterials aus dem Recken und Entspannen im Bereich von 6 bis 8 liegt.
9. Verfahren nach einem der Ansprüche 1 bis 8, worin das doppeltgereckte Filament im Ausmaß von 0,8x bis 0,9x entspannt wird.

Revendications

1. Procédé en ligne pour produire une suture de polypropylène comprenant les étapes consistant :
 - (a) à extruder une résine de polypropylène fondue à travers un orifice et à tremper rapidement la résine de polypropylène fondue pour produire un filament ;
 - (b) à étirer le filament dans la gamme de 4x à 7,5x dans une première zone d'étirage pour produire un filament étiré ;
 - (c) à étirer le filament simplement étiré dans une deuxième zone d'étirage dans la gamme de 1,0x à 2,5x tout en étant maintenue dans une seconde zone chauffée à une température dans la gamme de 30°C à 160°C, pour former un filament doublement étiré ;
 - (d) à relaxer et à recuire le filament doublement étiré dans la gamme de 0,75x à 0,95x, dans une troisième zone chauffée maintenue à une température dans la gamme de 100°C à 180°C, pour former une suture de polypropylène recuite.
2. Procédé selon la revendication 1, dans lequel le filament dans la première zone d'étirage est exposé à une première zone chauffée maintenue à une température dans la gamme de 30°C à 170°C.
3. Procédé selon la revendication 2, dans lequel la première zone chauffée est maintenue à une température dans la gamme de 40°C à 140°C.
4. Procédé selon l'une quelconque des revendications 1 à 3, dans lequel la deuxième zone chauffée est maintenue

à une température dans la gamme de 75°C à 140°C.

5. Procédé selon l'une quelconque des revendications 1 à 4, dans lequel le filament est étiré dans une étape unique dans la première zone d'étirage.
6. Procédé selon la revendication 5, dans lequel le filament est étiré par un premier et un deuxième guide-fils de filage chauffé.
7. Procédé selon l'une quelconque des revendications 1 à 6, dans lequel le filament simplement étiré est étiré dans la gamme de 1,06x à 1,9x dans la deuxième zone d'étirage.
8. Procédé selon l'une quelconque des revendications 1 à 7, dans lequel le rapport d'étirage total de la suture provenant de l'étirage et de la relaxation est dans la gamme de 6 à 8.
9. Procédé selon l'une quelconque des revendications 1 à 8, dans lequel le filament doublement étiré est relaxé dans la gamme de 0,8x à 0,9x.



THIS PAGE BLANK (USPTO)